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(54) Title: TREATING METAL SURFACES

(57) Abstract

A metal treatment composition comprises silica, one or more organo–phosphonates (or organo–phosphonate species) and/or one or more organo–phosphates (or organo–phosphate species), together with a carrier. The composition can be applied to the surface of a metal to enhance the resistance of the metal to corrosion and/or to enhance the adhesion to the treated metal of further coatings.

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TREATING METAL SURFACES

The present invention relates to a composition for treating metal surfaces, to a process for treating metal surfaces with the composition and to metal surfaces treated by means of such a process.

Metal surfaces are prone to corrosion, which weakens the strength of the metal over a period of time. There are many products available which help prevent the corrosion of metals. In many cases, however, the product is specific for one metal and therefore must be changed with the metal, which can lead to waste and cross-contamination.

Many known coating compositions contain chromium compounds. However, there is increasing pressure to remove chromium compounds from metal pretreatments and there are a number of known chromium-free processes. These known processes tend to be complicated and to require the use of catalysts and accelerators to speed up the coating process. The catalysts and accelerators may also need to be varied according to the metal surface.

Subsequent to treatment with a corrosion inhibitor, the metal surface often has one or more further coatings (e.g. paint) applied thereto and accordingly the coating composition should permit or promote good adhesion of such further coatings.

Our published European Patent Specification EP-B-0273698 discloses a composition for treating metal surfaces, in which the composition comprises a dispersion of silica in an aqueous solution of an acidic iron or aluminium compound.

Our co-pending application No. GB 9826851.9 discloses another composition for treating metal surfaces, in which the composition includes one or more organo-phosphonates or organo-phosphonate species.

We have now found that a metal treatment composition which includes both silica and one or more organo-phosphonates or organo-phosphonate species can be used to treat metal surfaces of all kinds to enhance the resistance of the metal to corrosion and/or to enhance the adhesion to the treated metal of further coatings.

We have further found that the composition according to the present invention can include one or more organo-phosphates or organo-phosphate species.

Accordingly, the present invention provides a composition suitable for use in the treatment of metal surfaces, the composition comprising silica, one or more organo-phosphonates or organo-phosphonate species **and/or** one or more organo-phosphates or organo-phosphate species, together with a carrier for the composition.

Preferably, the silica is of small particle-size.

Amorphous silica, which has been obtained pyrogenically from silicon tetrachloride, or which has been precipitated in an aqueous medium from alkali silicates, may be used. Thus, the silica is usually hydrophilic, non-crystalline and colloidal. The silica particles usually have an average particle size of less than 170 nm, but may have a particle size in the range 1-200 nm, preferably 1-50 nm, for example 4-30 nm and especially 8-20 nm.

The organo-phosphonate or organo-phosphonate species included in the composition of the present invention may be a mono-or di-phosphonic acid, ester or salt, especially with one or more unsaturated carbon-to-carbon bonds.

The phosphonic acid may thus be an alkyl, aryl or alkenyl phosphonic acid such as octyl phosphonic acid, phosphonosuccinic acid, phosphonopropanoic acid, vinylphosphonic acid (VPA), vinylidene-1, 1-diphosphonic acid (VDPA) or phenyl VPA.

The organo-phosphonate or organo-phosphonate species may comprise a polymer with pendant phosphonic or di-phosphonic acid groups.

Thus, the composition may include a homopolymer of a phosphonic acid such as vinylphosphonic acid (VPA), vinylidene-1, 1-diphosphonic acid (VDPA), phenyl VPA, or a salt or an ester of any of the said acids.

Alternatively, the composition may include a copolymer of a phosphonic acid (or a salt or an ester of said acid) together with a second co-monomer.

The second co-monomer may be an unsaturated carboxylic acid, such as acrylic acid, maleic acid or methacrylic acid (or salts or esters of any of the said acids).

The second co-monomer may alternatively be an unsaturated sulphonic acid, such as vinylsulphonic acid (VSA), or acrylamido methyl propane sulphonic acid (AMPS), (or an ester or a salt of any of the said acids).

The second co-monomer may be any other unsaturated compound (such as acrylonitrile) which is co-polymerisable with the phosphonic acid.

Again, the composition may include a terpolymer of an unsaturated phosphonate species and other suitable comonomers such as an unsaturated sulphonic acid, an unsaturated carboxylic acid or acrylamide.

For example, the composition may include a terpolymer of VPA, VSA and acrylic acid.

Alternatively the composition may include a polyester containing pendant phosphonic acid groups.

The organo-phosphate or organo-phosphate species included in the composition of the present invention may be an alkylene acrylate phosphate monomer, oligomer or homopolymer. Suitable alkylene acrylate phosphates include ethylene methacrylate phosphate.

Alternatively, the alkylene acrylate phosphates can be present in the composition of the present invention as copolymers, for example copolymers with unsaturated acids such as acrylic acid, methacrylic acid and salts and esters of these acids.

The ratio of silica to the organo-phosphonate **and/or** organo-phosphate in the compositions of the present invention must be such as to ensure a coherent coating with adequate covering properties.

The most convenient material for use as a carrier for the composition is water.

The present invention also provides a process for treating metal surfaces with compositions as hereinabove described, in which the process includes the steps of (a) making a composition according to the present invention,

(b) applying the composition to a metal surface and (c) causing or permitting the so-applied composition to dry to form an adherent coating on the metal surface.

Step (a) of the process may conveniently be carried out by dispersing the silica in water by means of a high-speed disperser and mixing into the dispersion the organo-phosphonate or organo-phosphate component.

Step (b) may be carried out by painting, dipping, spraying or roller-coating the composition on to the metal surface to be treated.

In accordance with one embodiment of the process of the present invention, the amount of composition to be applied to the metal surface may be controlled by dilution of the composition and adjustment of the wet film thickness.

Preferably the amount of composition residue left on the surface after drying is in the range of 0.001g/m^2 to 10.000g/m^2, more preferably 0.005g/m^2 to 5.000g/m^2 and most preferably 0.01-1.00g/m^2.

The composition may be applied to the metal surface by flood-spraying or immersion, the wet film being preferably metered to the required thickness (for example by means of one or more sets of squeegee rollers). The excess composition may be recovered and reused. Alternatively, the composition may be applied by roller-coating onto the metal surface. Roller-coating gives a more uniform coating than flood-spraying followed by squeegeeing and avoids waste of the composition.

In accordance with a second embodiment of the process of the present invention, the amount of composition to be applied to the metal surface may be controlled by a reaction occurring between the metal surface and the composition.

Preferably the surface is immersed in the composition, or an aqueous solution thereof, suitably for between 0.5 seconds and five minutes at a temperature of between 5°C and 100°C.

The metal surface may be wiped or rinsed after contact with the composition to remove any unbound composition.

The composition is preferably applied as an aqueous solution.

Step (c) may be carried out by allowing the composition to dry passively at ambient temperature. Alternatively, the composition may be dried positively at a temperature of 60-200°C for 0.1-10 minutes, preferably at 80-180°C for 0.1-5 minutes, for example at 140-180°C for 0.5-2 minutes.

The process according to the present invention is applicable to any metal surface.

The metal surface to which the composition is to be applied may be pre-cleaned, for example by treatment with an aqueous acid or alkaline degreasing preparation and brushing.

The metal surface to which the composition has been applied may be wiped or rinsed.

The advantages of these methods of application of the composition include the uniform application of the composition to the metal surface, the low capital cost and the possibility of recycling excess composition to avoid waste.

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The present invention further provides a metal surface treated by the process described hereinabove.

CLAIMS

1. A composition suitable for use in the treatment of metal surfaces, the composition comprising silica, one or more organo-phosphonates or organo-phosphonate species and/or one or more organo-phosphates or organo-phosphate species, together with a carrier for the composition.

2. A composition according to Claim 1, in which the silica has an average particle size of less than 170nm.

3. A composition according to Claim 2, in which the silica has an average particle size of 1-200nm.

4. A composition according to Claim 2 or 3, in which the silica has an average particle size of 1-50nm.

5. A composition according to Claim 2, 3 or 4, in which the silica has an average particle size of 4-30nm.

6. A composition according to any one of Claims 2 to 5, in which the silica has an average particle size of 8-20nm.

7. A composition according to any one of Claims 1 to 6, in which the organo-phosphonate or organo-phosphonate species is a mono - or di-phosphonic acid, ester or salt.

8. A composition according to Claim 7, in which the organo-phosphonate or organo-phosphonate species is an alkyl, aryl or alkenyl phosphonic acid.

9. A composition according to Claim 8, in which the phosphonic acid is octyl phosphonic acid, phosphono-succinic acid, phosphono-propanoic acid, vinylphosphonic acid (VPA), vinylidene-1,1-diphosphonic acid (VDPA) or phenyl VPA.

10. A composition according to any one of Claims 1 to 6, in which the organo-phosphonate or organo-phosphonate species comprises a polymer with pendant phosphonic or di-phosphonic acid groups.

11. A composition according to Claim 10, in which the organo-phosphonate or organo-phosphonate species comprises a homopolymer of VPA, VDPA, phenyl VPA or a salt or an ester of any of said acids.

12. A composition according to any one of Claims 1 to 6, in which the organo-phosphonate or organo-phosphonate species comprises a copolymer of a phosphonic acid (or a salt or an ester of said acid) together with a second comonomer.

13. A composition according to Claim 12, in which the second comonomer is an unsaturated carboxylic acid.

14. A composition according to Claim 12 or 13, in which the second comonomer is acrylic acid, maleic acid or methacrylic acid (or a salt or an ester of any of said acids).

15. A composition according to Claim 12, in which the second comonomer is an unsaturated sulphonic acid.

16. A composition according to Claim 15, in which the second comonomer is vinyl sulphonic acid (VSA), acrylamido methyl propane sulphonic acid (AMPS) or an ester or a salt of either of said acids.

17. A composition according to Claim 12, in which the second comonomer is acrylonitrile.

18. A composition according to any one of Claims 1 to 6, in which the organo-phosphonate or orgno-phosphonate species comprises a terpolymer of an unsaturated phosphonate and two comonomers selected from the group consisting of unsaturated sulphonic acids, unsaturated carboxylic acids and acrylamide.

19. A composition according to Claim 18, in which the terpolymer is a terpolymer of VPA, VSA and acrylic acid.

20. A composition according to any one of Claims 1 to 6, in which the organo-phosphonate or organo-phosphonate species comprises a polyester containing pendant phosphonic acid groups.

21. A composition according to any one of the preceding claims, in which the organo-phosphate or organo-phosphate species is an alkylene acrylate phosphate monomer, oligomer or homopolymer.

22. A composition according to Claim 21, in which the alkylene acrylate phosphate is ethylene methacrylate phosphate.

23. A composition according to any one of Claims 1 to 20, in which the organo-phosphate or organo-phosphate species is a copolymer

of an alkylene acrylate phosphate with an unsaturated acid (or a salt or ester of such an acid).

24. A composition according to Claim 23, in which the unsaturated acid is acrylic acid or methacrylic acid.

25. A composition according to any one of the preceding claims, in which the carrier is water.

26. A process for treating metal surfaces with a composition according to any one of Claims 1 to 25, said process comprising the following steps:

(a) making said composition by dispersing the silica in water and mixing into the dispersion the organo-phosphonate or organo-phosphate component;

(b) applying said composition to a metal surface;

(c) causing or permitting the so-applied composition to dry to form an adherent coating on said metal surface.

27. A process according to Claim 26, in which step (b) is carried out by painting, dipping, spraying, or roller-coating the composition on to the metal surface.

28. A process according to Claim 26 or 27, in which the amount of composition residue left on the metal surface after drying is in the range 0.001 g/m^2 to 10.000 g/m^2.

29. A process according to Claim 28, in which the amount of composition residue left on the metal surface after drying is in the range 0.001 g/m² to 5.000 g/m².

30. A process according to Claim 28 or 29, in which the amount of composition left on the metal surface is in the range 0.01 g/m² to 1.00 g/m²..

31. A process according to any one of Claims 26 to 30, in which the metal surface is immersed in the composition or an aqueous solution of said composition for between 0.5 seconds and 5 minutes at a temperature of between 5°C and 100°C.

32 A process according to any one of Claims 26 to 31, in which step (c) is carried out by allowing the composition to dry passively at ambient temperature.

33. A process according to any one of Claims 26 to 31, in which step (c) is carried out by drying the composition at 60°C to 200°C for 0.1 to 10 minutes.

34. A process according to Claim 33, in which the composition is dried at 80°C to 180°C for 0.1 to 5 minutes.

35. A process according to Claim 33 or 34, in which the composition is dried at 140°C to 180°C for 0.5 to 2 minutes.

36. A process according to any one of Claims 26 to 35, in which the metal surface is pre-cleaned before step (b).

37. A process according to Claim 36, in which the pre-cleaning of the metal surface is carried out by means of treatment with an aqueous acid or alkaline de-greasing preparation, followed by brushing.

38. A process according to any one of Claims 26 to 37, in which, after stage (c), the coated surface is wiped or rinsed.

39. A process according to Claim 26, substantially as hereinbefore described.

40. A metal surface which has been treated by a process according to any one of Claims 26 to 39.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/GB 00/00611

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C22/68 C09D5/08 C09D143/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C23C C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 351 675 A (GUHDE DONALD J) 28 September 1982 (1982-09-28) column 5, line 66 -column 8, line 40	1-7, 25-27, 31-35, 37,40
X	WO 95 04169 A (HENKEL CORP) 9 February 1995 (1995-02-09) example 17B	1-7, 25-30, 32-37,40
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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